

PATENT ABSTRACTS OF JAPAN

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(54) THICK-FILM PASTE COMPOSITION

(57)Abstract:

PURPOSE: To provide such a thick-film paste composition as provides required superior film forming performance, drying paint film strength, and shape stability despite of changes in applied environment, by distributing a mixture of finely divided active metal, etc., in an inactive liquid vehicle containing hydroxypropyl cellulose.

CONSTITUTION: A thick-film paste composition is so constituted that a mixture of, at least, active metal of a finely divided form or a nonmetal conductive material and/or inorganic binder is distributed in an inactive liquid vehicle containing hydroxypropyl cellulose(HPC). The used inactive liquid vehicle is that HPC 5 to 25wt.% is dissolved in, for example, solvent 75wt.% such as butyl carbytol or terpeneol. As for content of HPC in all paste composition, 6 to 80wt.% of inorganic solid is used per HPC 1wt.% to stabilize printing workability and point film physical property such as drying strength of thick- film paste.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application]This invention relates to a thick-film-paste constituent and the constituent which uses an especially new inert liquid object-like vehicle.

[0002]

[Description of the Prior Art]The thick film constituent containing the active metal or the conductive substance, and/or inorganic powder which were distributed in the vehicle which consists of a volatile organic solvent and resin, It is used in order to form a microcircuit by being applied on a dielectric substrate (glass, glass ceramics, and ceramics), and being calcinated. This thick film constituent contains the inorganic powder (for example, metal particles and/or binding material particles) by which detailed division was usually carried out, and distributes these inorganic powder in an inert liquid object-like medium or a vehicle. the metal and/or the inorganic powder ingredient in this constituent give functional usefulness (a conductor, a resistor, or a dielectric) -- on the other hand -- an inorganic binder (for example, glass and a crystalline oxide -- in addition) -- metal particles -- mutual -- and it is made to combine with a substrate The thick film technique of the thin film technology which includes deposition of the particles by evaporation or sputtering is contrastive. Thick film technique is discussed by Handbook of Materials and Process for Electronics for Mr. [C.A. Harper] of Chapter 12 (McGraw-Hill1970 edition).

[0003]The paste Mr. constituent which mixes an inorganic particle with an inert liquid object medium (vehicle) by mechanical mixing (for example, on a roll mill), and has the suitable consistency and rheology for screen-stencil is generated. By the usual method, it can print as a film on ceramics, such as an alumina substrate, or other dielectric substrates by using this paste composition as a "thick film."

[0004]Conventionally, any one of the water which added a thickening agent, stabilizer, and/or

other common additive agents, or is not adding these, or the various organic fluids is used as a vehicle. As an organic fluid which can be used, ester, for example, the acetate, and propionate of fatty acid alcohol and such alcohol, They are a solution of resin, for example, the polymethacrylate of lower alcohol, in a terpene, for example, wood turpentine oil, a terpeneol and others, a solvent, for example, wood turpentine oil, and the monobutyl ether of ethylene glycol mono- acetate, or a solution of ethyl cellulose. Content or the vehicle can also comprise this in the volatile fluid for making a vehicle promote the quick solidification after application to a substrate. A common vehicle uses ethyl cellulose and a beta terpeneol as a base.

[0005] Vehicles are the application characteristic of a constituent, and a thing which affects especially the rheology as above-mentioned.

To have low viscosity is desired in order that it can acquire a suitable consistency and rheology to apply on a substrate.

Generally the printing pattern which may be simultaneously applied on a substrate is neglected and leveled, and good covering is attained by being dried and calcinated.

Viscosity of enough thick-film-paste constituents to hold the film moldability after this screen-stencil is desired.

It is desirable that the rheology was not influenced with temperature and it is stable irrespective of change of application environment.

[0006] However, the constituent paste which made the organic vehicle containing conventional ethyl cellulose distribute a part for an inorganic solid, and was generated has the problem (gap) which used screen stencil art and was applied on the substrate and which the shape of a printing pattern film will transform by the time it is back-calcinated. The method of adjusting the viscosity was conventionally performed widely by a paste composition adjusting rheology using an organic medium, and obtaining desired printing viscosity, or limiting the quantity of resin or adding other substances for volatile adjustment. However, the viscosity of the paste composition adjusted in this way also receives open air environmental influence in a screen printing stage, especially it is known that the influence on the viscosity by temperature is size. Therefore, when it prints to a substrate using the paste composition which specified the content of the vehicle by which viscosity control was carried out eventually by the method known conventionally, a problem is produced in print job nature and a printing characteristic. There was evil to which the dry paint film intensity of an after-printing pattern formation film falls by addition of other above-mentioned substances. In the microcircuit formation using thick film technique, the morphological stability of the coat of a paste composition is required from the tendency of the formation of thin smallness of a printing pattern, and densification against such the actual condition in recent years.

[0007]

[Problem(s) to be Solved by the Invention] Therefore, the purpose of this invention cancels the

relation as which it originates in organic vehicle use of ethyl cellulose in the conventional thick-film-paste constituent, and the dissatisfied viscosity characteristic of a paste composition is determined, The paste composition provides the thick-film-paste constituent to which the outstanding film moldability, dry paint film intensity, and morphological stability which are required of a substrate in the thick film formed by application and application by screen-stencil etc. are given in spite of change of application environment.

[0008]

[Means for Solving the Problem]The above-mentioned purpose is attained by thick-film-paste constituent which made an inert liquid object-like vehicle containing hydroxypropylcellulose (it is hereafter called HPC for short) distribute an active metal of a gestalt and a mixture of an inorganic binder by which detailed division was carried out at least. Print job nature and film properties outstanding with a thick-film-paste constituent which contains a part for an inorganic solid of six to 180 weight section per HPC 1 weight section can be provided. This invention is explained still in detail below.

[0009]In this invention, powder, such as silver dust, copper powder, aluminum, and nickel, carbon, graphite, carbon fiber, silver plating particles, ruthenium oxide powder, gold dust, etc. can be used as an active metal, for example. Silver dust is chemically stable and, moreover, can be preferably used for an electrical part which attaches importance to reliability for high conductivity. Powder, such as copper, aluminum, and nickel, carbon powder, graphite, and carbon fiber can be preferably used according to the purpose, although it is necessary to take into consideration the ease of winning popularity of oxidation, conductive stability, moisture resistance, etc. What carried out silver plating can be used for particles, such as carbon powder, copper powder, nickel powder, and a glass bead, as an activity phase of a constituent in this invention. Gold dust is built from a gold chloride using a chemical reaction, or is built using gold foil. Gold dust is chemically stable and has high conductivity. In addition, as a conductive substance, an alloy and mixtures, such as Pd/Ag, Pd/Ag, and Pd/Au, can also be used. A conductive substance is chosen with a performance characteristic for which a paste composition is asked, for example, resistivity, shift resistance, an adhesive property, either of the other one, or specific combination. In this invention, a conductive substance is used with a gestalt of a detailed split particle.

[0010]In this invention, glass frit, a bismuth compound, zinc and/or a zinc compound, nickel and/or a nickel compound, and an alkaline earth metal compound can be used as an inorganic binder. Glass of a low softening point and hypoviscosity is preferred. In this invention, glass mixed by a ratio of a request of 1 or 2 or more glass frits which consist of ingredients chosen from PbO, SiO₂, and B₂O₃, aluminum₂O₃, TiO₃, and ZnO can be used. In this invention, material which constitutes inorganic binders, such as these glass, is used with a gestalt of a detailed split particle.

[0011]Functional material powder which is the formed elements which contain a thick-film-paste constituent according to a difference in functional usefulness provided in circuit formation differs. That is, in the case of conductive paste, in the case of metal powder, inorganic binder powder, such as glass, and resistive paste, inorganic powder which consists of glass, an oxide, etc. is contained as a functional material in the case of a conductive substance, inorganic binder powder, and dielectric paste. An ingredient rate of a vehicle which dissolved a conductive component, an inorganic joint ingredient, and resin solid content like HPC by this invention into a solvent about each paste, and a solvent is shown as follows. A number is weight % unless it mentions specially.

[0012]

(1) 導体ペースト

成 分	重量%
導電性粉末 (銀、銅等)	50～90
無機結合剤粉末 (ガラス、酸化物等)	0.5～18
ビヒクル	5～40
溶 剤	3～20

(2) 抵抗体ペースト

成 分	重量%
導電性粉末 (酸化ルテニウム等)	1～30
無機結合剤粉末 (ガラス、酸化物等)	25～80
ビヒクル	5～40
溶 剤	3～20

(3) 誘電体ペースト

成 分	重量%
無機結合剤粉末 (ガラス、酸化物等)	60～85
ビヒクル	5～35
溶 剤	3～20

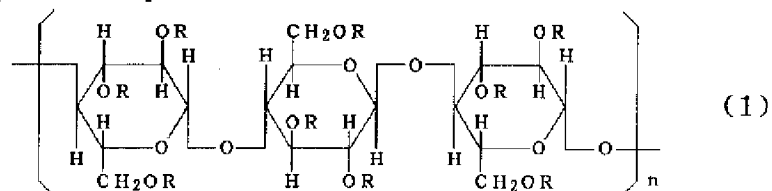
[0013]An inert liquid object-like vehicle by this invention dissolves 5 to 25 % of the weight of HPC(s), for example in butylcarbitol or 75 to 95 % of the weight of solvents like terpineol. About content in all the paste compositions of HPC, a part for an inorganic solid of six to 180 weight section is used per HPC 1 weight section from the purpose of stabilizing film properties, such as the print job nature of thick film paste, and baked strength. If a rate ratio for HPC and an inorganic solid is in this range, it is also possible to add other resin solid content, such as ethyl cellulose, rosin, phenol resin, and a wax. If a part for an inorganic solid is made into less than six weight sections per HPC 1 weight section, viscosity of a paste composition will become high too much, and print job nature will get worse. If a part for an inorganic solid is made into 180 weight sections per HPC 1 weight section, dry paint film intensity will become insufficient.

[0014]An organic vehicle in this invention consists of hydroxypropyl ether of cellulose of a non-

ion system fibrin derivative produced by making propylene oxide react to cellulose expressed with about 5 dissolved into a non-hydrocarbon polar solvent - a following general formula (1) of 25 % of the weight of abbreviation intrinsically.

[0015]

[Formula 1]



構造式中のR : Hまたは $(-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{O})_m$ H基を表わし

mは1以上の整数

For example, the Nisso hydroxypropylcellulose by Nippon Soda Co., Ltd. (trade name: Nisso HPC) can be used.

[0016]The hydroxypropylcellulose (HPC) typically used into the organic medium of this invention is very a thermoplastic high substance, and it is known that the following outstanding characteristics are shown.

- Film formation nature, unity, thickening nature, dispersibility, and emulsion stability - It is inertness harmless and chemically. [0017]The solvent component of this invention is a non-hydrocarbon polar solvent, and this may dissolve thoroughly the line aromatic-polyester-resin ingredient of an organic medium. This solvent is fully volatility, and as a result, below at the pyrolysis temperature of a flexible substrate, it is evaporated from a constituent and you have to sell it. As such a substance, ester, alcohol, ether, and a halogenated aromatic compound are raised. Although it is completely operational in this invention in a halogenated aromatic compound, for example, dichlorobenzene, they are not preferred on account of the danger of following on them and of receiving healthily. As a suitable solvent, therefore, ethylene glycol phenyl ether, benzyl alcohol, Glycol ether acetate, carbitol acetate, butyl Cellosolve acetate, butylcarbitol, butylcarbitol acetate, and a substance like terpeneol are raised. Especially carbitol acetate is preferred. it is used by the mixture of various solvents for volatile adjustment of the solvent component of an organic medium, carrying out by being alike occasionally.

[0018]Generally the boiling point of a solvent component should not be about 150 °C or less. A 150-250 °C boiling range is preferred. A solvent which has the boiling point about 150 °C or less tends to make a constituent thicken too much between screen-stencil for the evaporation. This can bring a result which produces blinding of a screen used in order to print a pattern of a substance on a substrate, of course. However, solvent volatility will be chosen in consideration of solvent removal and/or a molding method within this limit. For example, when the high-speed reel method is used, it is important that a solvent is removed very promptly between

processings. That is, what is boiled at a solvent of the lower boiling point, for example, 150-175 **, must be used. On the other hand, when a later molding method is used, a volatile smaller solvent, for example, a thing of the 175-250 ** boiling point, is used. In both cases, solvent removal is promoted by usually heating a printing substrate mildly. Typically, a substrate is heated by 90-120 **, 70-90 ** and when a more volatile solvent is used by the reel reel method in hot wind oven, and a volatile small solvent is used more by a semi-automatic method again. [0019] Usually, as balance (remainder) of an after [load] medium of resin, a solvent exists in an organic medium. However, unless change is given to essence of an organic medium, an additive agent of a little others can be added. Especially when an organic solvent cannot be used from an environmental problem etc., a paste can also be manufactured with a vehicle which dissolved HPC in water. In this case, the range of an inorganic substance weight section per HPC 1 weight section presupposes that it is equivalent to a case where an organic solvent is used. A particle state inorganic solid is mixed with an organic medium in manufacture of a constituent of this invention, And make it distribute using a suitable device, for example, 3 roll mills, a suspended solid is made to generate, and a constituent of as [whose viscosity of the is the range of 50 - 450 _{PA-S} (it is the viscosity in ten rotations with the Brookfield HBT type four sheet viscosity meter) by that cause] is made to generate.

[0020] Next, measurement about a viscosity ratio, a temperature change of viscosity, combustion ease, and dry paint film intensity and a test method are explained, respectively. (A) Viscosity and a viscosity-ratio Brookfield HBT type, and spindle No.14 are used, A paste composition is put into a utility cup, a spindle is set during a paste so that air bubbles may not be bound, and low Schar viscosity (0.5 rpm) and quantity Schar viscosity (10 rpm) are measured, and let what broke a low Schar viscosity value by a quantity Schar viscosity value be a viscosity ratio. About viscosity, a paste is set to a viscosity meter and viscosity when changing temperature of a paste composition to 20 **, 25 **, and 32 ** respectively is measured.

[0021] (B) Although the degree of sintering of resolvability's of resin material in paste composition electric conduction particles at the time of calcination and a softened state of glass are affected at a general combustion ease target, the influence is great to especially resistance of a thick film resistor and a temperature coefficient (HTCR). Therefore, in investigating the flammability of resin, influence on an electrical property as a resistor is investigated to resistive paste using hydroxypropylcellulose. Resistance and HTCR at calcination temperature of 800 **, 850 **, and 900 ** are measured, respectively.

(C) Print a paste on a dry paint film intensity alumina substrate, scratch the dry surface by a core of a pencil of hardness of 1H-9H after 10-minute desiccation at 150 **, and measure hardness of a pencil which gave a crack to the surface.

[0022] According to the thick-film-paste constituent of this invention, a thick-film-paste

constituent which gives an outstanding film moldability, dry paint film intensity, and morphological stability which are required of a substrate in spite of change of application environment in a thick film formed by application and application by screen-stencil etc. can be obtained.

[0023]

[Example]Next, an example and a comparative example are given and explained about this invention. As the constituent given in an example and a comparative example was described above on these specifications, it is manufactured, and it is measured and examined. The number showing an ingredient rate is weight % unless it mentions specially. This invention does not receive restriction at all according to this example. A result is shown in Table 1. 20% of the ruthenium oxide powder and the glass binding material (34.0 % of the weight of SiO_2) which have the grain size of about 1 micrometer - the about 10-micrometer range 1.0 % of the weight of $\text{aluminum}_2\text{O}_3$, and PbO 65.0 % of the weight 40 % of the weight, It was made to distribute in the vehicle which contains 6 % of the weight of polyester resin, and 30 % of the weight of beta-terpineols as resin other than 4 % of the weight of HPC(s), and HPC, this was kneaded by 3 roll mills, and the paste composition was adjusted. The weight ratio of the inorganic solid content (silver dust + glass binding material) opposite vehicle in a constituent was 60/40. The pattern obtained by adjusting as mentioned above and applying a thick-film-paste constituent by screen-stencil on an alumina substrate was calcinated at 800 **, 850 **, or 900 **, and the thick film was formed. This thick film is measured and evaluated about the temperature change, combustion ease, and dry paint film intensity of viscosity, and that result is shown in Table 1.

[0024]In the comparative example, ethyl cellulose was used instead of HPC used in the example, and the thick-film-paste constituent and the calcination thick film were manufactured and formed like the procedure of an example with the presentation shown in Table 1. The measurement same about the thick film formed as mentioned above as an example and evaluation are performed, and the result is shown in Table 1.

[0025]As shown in Table 1, the example which contains HPC as a vehicle, Compared with the comparative example which uses ethyl cellulose as a vehicle, it has the same flammability, And prevent the temperature dependence of the paste viscosity at the time of using it for a paste, and, Since it had the intensity which can secure the stable printing nature and is the same as a status product also in dry paint film intensity, without receiving big influence in the environment at the time of printing since the viscosity ratio was also raised, it has checked not producing the separation of the coat in the process of operation after printing/desiccation, etc.

[0026]

[Table 1]

サ ン プ ル	温度	回 転 数	実 施 例	比 較 例
(A) ペーストの温度 変化による粘度 への影響	20℃	0.5	640	640
		10	176	296
		0.5/10	3.64	2.16
	25℃	0.5	540	460
		10	141	188
		0.5/10	3.83	2.45
	32℃	0.5	440	300
		10	105	105
		0.5/10	4.19	2.86
(B) 燃 焼 容 易 性	焼成温度			
	抵抗値 (kΩ)	800℃	39.39	33.54
		850℃	54.61	54.59
		900℃	57.19	60.52
	温 度 係 数 (ppm/℃)	800℃	+79	+103
		850℃	+24	+34
		900℃	-42	-37
(C) 乾 燥 塗 膜 強 度 Pad数=44 鉛筆でひっかい た後の剥離数	鉛 筆 硬 度			
	1H └ 6H		0	0
	7H		0	0
	8H		1	2
組 成	導 電 成 分		20	20
	ガ ラ ス 成 分		40	40
	セルロース以外 の樹脂		6	6
	セ ル ロ ー ス		H P C 4 wt%	エチルセルロース 4 wt%
	溶 剤		30	30
	合 計		100wt%	100wt%

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CLAIMS

[Claim(s)]

[Claim 1]A thick-film-paste constituent which a mixture of an active metal of a gestalt or a nonmetallic conductive substance, and/or an inorganic binder by which detailed division was carried out at least distributes to an inert liquid object-like vehicle containing hydroxypropylcellulose.

[Claim 2]The thick-film-paste constituent according to claim 1 containing a part for an inorganic solid of six to 180 weight section per hydroxypropylcellulose 1 weight section.

[Translation done.]